

## Research Article

# Simulation Experiment Study on Impacting the $\delta D$ Value of Aromatic Compounds

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Little is known about the effects of sedimentary environment and maturity on  $\delta D$  values of aromatic compounds deposited in geological bodies. Our simulation experiments showed that the  $\delta D$  value of pyrolytic polycyclic aromatic hydrocarbons (PAHs) was significantly different between the studied samples from high and low latitude regions. Comparative studies showed that the  $\delta D$  values of PAHs produced by pyrolysis were related to those of water in the two regions. With increasing maturity, the  $\delta D$  value of the PAHs becomes higher. Additionally, it was observed that some PAHs exhibited a propensity to increase the  $\delta D$  value upon demethylation. The thermodynamic fractionation of hydrogen isotopes between the PAHs produced by pyrolysis and both the *n*-alkanes and methane produced by pyrolysis indicated that the hydrogen isotopic value of the PAHs was higher than that of the *n*-alkanes or methane. The long-chain alkylbenzene produced by pyrolysis has a higher mean  $\delta D$  value compared with the *n*-alkanes produced by pyrolysis, but it is lower than that of the PAHs in the same sample. The lowest  $\delta D$  value among the aromatics was found in the ring A monoaromatic steroids produced by pyrolysis. The low  $\delta D$  values of these steroids should originate from isotopic fractionation during isoprenoid lipid biosynthesis.

## 1. Introduction

Aromatic compounds are a significant component of sedimentary soluble organic matter and contain rich information about the formation of sedimentary organic material. PAHs have been applied to evaluate organic matter sources, formation environment, maturity, and diagenetic alteration [1–9]. With the improvement of isotope analysis technology for individual organic molecule, the carbon isotopic analysis of individual PAHs has made its application more accurate and more extensive [10, 11] and played a significant role in environment and petroleum exploration research [11]. However, current research on the hydrogen isotope of individual hydrocarbon compounds mainly focuses on alkanes, particularly *n*-alkanes [12–16]. The  $\delta D$  value of sedimentary

*n*-alkanes has become an important indicator for evaluating paleoclimate environment, organic matter source, and maturity [17–21].

If the hydrogen isotopes of individual sedimentary aromatic compounds can keep track of the water origin during the precursor biosynthesis like *n*-alkanes [16], the hydrogen isotopic composition of individual sedimentary aromatic compounds can track the paleoclimate. At the same time, the hydrogen isotopes of individual sedimentary aromatic compounds should be related to their biological sources, sedimentary environment, and diagenetic evolution, so there is potential application in oil and gas geochemical research. However, there are only a few reports on the hydrogen isotope studies of individual aromatic compounds in geologic sediments. For example, Tuo et al. [22] determined the  $\delta D$

value of simonellite in coal and carbonaceous mudstone; Zhang et al. [23] studied the variations in the  $\delta D$  value of PAHs in modern sediments from the East China Sea and discussed their sources. Uncertainty persists regarding the factors influencing the  $\delta D$  values of the individual sedimentary aromatic compounds in geological bodies.

Peat, which has not undergone deep burial or strong degradation and generally contains abundant original organic content, is regarded as the original material of coal. In addition, the herbaceous peat-forming organisms are relatively simple, allowing us to easily understand the original organic matter in the peat. Therefore, in this study, we chose contemporary herbaceous peats formed under different sedimentary environments. Simulation experiment of these samples was carried out under anhydrous and closed conditions at 200°C–400°C, and the compound-specific  $\delta D$  analysis of individual aromatic compounds in pyrolysates was conducted. The characteristics of hydrogen isotope composition of aromatic compounds during the coalification of herbal peats from different latitude regions were investigated. The purpose of this research is as follows: (1) to identify the discrepancy in  $\delta D$  value of various types of aromatic compounds formed under different sedimentary environments and at different simulation temperatures; (2) to understand the discrepancy between the  $\delta D$  values of aromatic hydrocarbons and *n*-alkanes/methane by comparing with previous research results; (3) and to further understand the impact of sedimentary environment, thermal evolution, and compound type on the hydrogen isotopes of individual sedimentary aromatic compounds.

## 2. Samples and Analysis

The two samples used in the pyrolysis are all herbal peat. A sample with a latitude of 48° North was collected in the Altay area of Xinjiang, while another sample with a latitude of 21° North was taken in the Zhanjiang area of Guangdong, both in China. The samples had a depth between 1.5 and 3.0 m and had total organic carbon content (TOC) of 32.3% to 34.5%. Altay and Zhanjiang regions have elevations of 2560 m and 28 m, respectively, and their respective mean annual temperatures of -1.8 to 1.8°C and 23.4°C. The peat was dried to zero moisture at room temperature. The peat was then crushed and dried again naturally for several days.

Similar to those previously described, methods for peat pyrolysis, extraction, and instrumental analysis for aromatic compounds were used [24, 25]. In short, the experiment on the peat sealed in a quartz tube was conducted in a muffle furnace under anhydrous condition. Each sample was isothermally pyrolyzed at 200°C, 250°C, 300°C, 350°C, and 400°C for 72 h. The solid residues were collected and subjected to Soxhlet extraction with dichloromethane methanol (3:7, v:v). The extracts were separated into saturated hydrocarbons and aromatic hydrocarbons using column chromatography with *n*-hexane and CH<sub>2</sub>Cl<sub>2</sub> as eluting solvents. Gas chromatography–mass spectrometry (GC–MS) analyses of the aromatic compounds in the aromatic hydrocarbon fraction were carried using a Hewlett-Packard 6890 gas chromatograph interfaced to a Hewlett-Packard 5973 mass selective

detector. An HP-5 column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used. The GC oven temperature began at 80°C and then increased to 300°C at 3°C/min (held 30 min).  $\delta D$  values of the aromatic compounds were determined by gas chromatography (Thermo Scientific Trace)—isotope ratio mass spectrometric (Finnigan-MAT 253) analysis. The combustion furnace was at 1450°C. The analysis conditions of the gas chromatograph were analogous to the GC-MS except that the column was 60 m. In order to evaluate the reproducibility of the instrumental analysis, a mixture of standard components with known isotopic composition were measured several times prior to and following the sample runs. The H<sup>3+</sup> factor was determined after every five injections and was constant at about 7.0. In general, the amount required for hydrogen isotope analysis of aromatic compounds is relatively large. Due to the limitation of the amount of samples, the hydrogen isotope analysis of pyrolytic aromatic compounds cannot be repeated for more times like the analysis of *n*-alkanes. In order to ensure the accuracy of hydrogen isotope analysis, we repeated the analysis of saturated hydrocarbon fractions with sufficient amount before the analysis of aromatic fractions. When the standard deviation of hydrogen isotope analysis of saturated hydrocarbon fraction was less than 5‰, the hydrogen isotope analysis of aromatic fraction produced by pyrolysis was carried out.  $\delta D$  values (‰ relative to the VSMOW reference standard) of one to three analyses with a standard deviation of <5‰ are reported for all aromatic compounds.

## 3. Results

**3.1. Composition of Aromatic Compounds.** The PAHs were not detected in the aromatic hydrocarbon fractions produced by pyrolysis at 200°C and 250°C, and only a few trace PAHs were detected in the aromatic hydrocarbon fraction at 300°C. However, at 350 and 400°C, the PAHs in the two peat samples are the most abundant. In this study, PAHs only involved the experimental results at 350°C and 400°C for comparative research. The analysis results of the PAHs were shown in Table 1. The PAHs pyrolyzed by the Altay peat at 350°C and 400°C (named 350Alt and 400Alt samples) were composed of fluorene, dibenzofurans, phenanthrene, anthracene, acephenanthrene, pyrene, chrysene, and their alkyl homologs, as well as fluoranthene, benzo[*c*]acridine, and benzo[*a*]anthracene, which were tri- and tetracyclic aromatic compounds. Phenanthrene and alkyl phenanthrenes made up the majority of the aromatic compounds in the 350Alt and 400Alt samples, accounting for 53.2% and 59.4%, respectively. Alkyl fluorenes and alkyl dibenzofurans came in second and third, accounting for 15.4% and 14.6%, respectively. Other PAHs were relatively low in abundance (Table 1). In addition, the 350Alt and 400Alt samples contained long-chain alkylbenzenes. The long-chain alkylbenzenes are composed mainly of the long-chain homologs (C<sub>25</sub>–C<sub>36</sub>) with a modal distribution, maximizing at C<sub>28</sub> (Figure 1 and Table 2). The liquid hydrocarbon pyrolyzed by the Altay peat at 250°C (named 250Alt sample) contained C<sub>27</sub>, C<sub>28</sub>, and C<sub>29</sub> ring A monoaromatic steroids, with C<sub>29</sub> as the main peak (Figure 2). Their molecular structure and mass

TABLE 1: Relative abundance of aromatic compounds in the pyrolysis samples.

Temperature (°C)	Sample no.	AFs (%)	ADBFus (%)	P (%)	MPs (%)	DMPs (%)	TMPs (%)	TeMPs (%)	A (%)	MA (%)	APa (%)	MAPas (%)	Py (%)	MPys (%)	DMPys(%)	Chy (%)	MChys (%)	DMChys (%)	Other (%)	Benzpy
350	350Alt	6.4	9.0	1.1	11.6	30.7	9.8	No	0.7	3.3	1.7	7.0	2.6	5.4	No	0.8	1.7	0.8	7.5	No
400	400Alt	7.4	7.2	2.8	24.1	28.0	4.5	No	3.1	6.3	2.8	4.7	3.4	3.4	No	No	No	No	2.2	No
350	350Zwx-3	0.8	4.5	3.2	11.8	24.0	8.2	5.0	0.7	1.6	0.7	No	2.5	8.7	5.5	1.0	3.0	2.7	1.2	1.72
400	400Zwx-3	0.9	1.8	3.4	17.6	16.7	9.0	No	0.8	No	5.5	No	12.3	8.3	2.6	5.1	4.0	No	8.7	3.26

ANas: alkyl naphthalenes; AFs: alkyl fluorenes; ADBFus: alkyl dibenzofurans; P: phenanthrene; MPs: methylphenanthrenes; DMPs: dimethylphenanthrenes; TMPs: trimethylphenanthrenes; TeMPs: tetramethylphenanthrenes; A: anthracene; MA: methylanthracene; APa: acphenanthrene; MAPas: methylacephenanthrenes; Py: pyrene; MPys: methylpyrenes; DMPys: dimethylpyrenes; Chy: chrysene; MChys: methylchrysenes; DMChys: dimethylchrysenes; other: fluoranthene, benz[c]acridine, and benz[a]anthracene; Benzpy: benzopyrene; No: not detected.

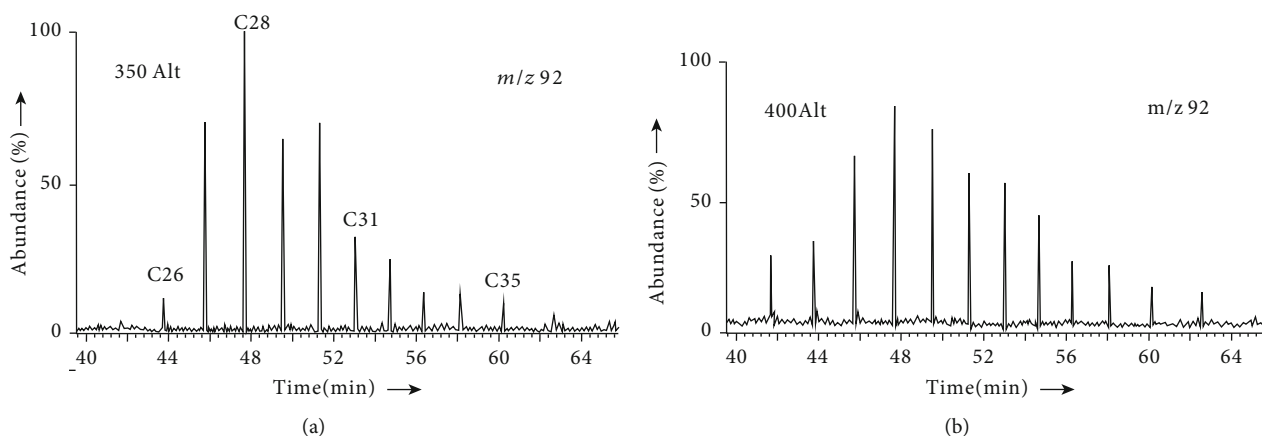


FIGURE 1: Molecular distributions of long-chain alkylbenzene in the 350Alt (a) and 400Alt (b) samples.

TABLE 2: Parameters of long-chain alkylbenzenes in the pyrolysis samples.

Compound	Sample no.	C <sub>range</sub>	C <sub>max</sub> <sup>a</sup>	C <sub>25</sub> <sup>-</sup> /C <sub>25</sub> <sup>+b</sup>	ACL <sup>c</sup>	CPI <sup>d</sup>
Alkylbenzene	350Alt	C <sub>25</sub> -C <sub>36</sub>	C <sub>28</sub>	Very low	28.8	0.87
Alkylbenzene	400Alt	C <sub>25</sub> -C <sub>36</sub>	C <sub>28</sub>	Very low	28.9	1.13
Alkane	350Alt	C <sub>15</sub> -C <sub>31</sub>	C <sub>21</sub> , C <sub>27</sub>	2.98	26.6	1.31
Alkane	400Alt	C <sub>16</sub> -C <sub>30</sub>	C <sub>21</sub>	4.60	26.5	1.22

<sup>a</sup>Peak carbon number; <sup>b</sup>long-chain/short-chain:  $\leq nC_{25}/>nC_{25}$ ; <sup>c</sup>average chain length =  $[25(nC_{25}) + 27(nC_{27}) + 29(nC_{29}) + 31(nC_{31}) + 33(nC_{33})]/(nC_{25} + nC_{27} + nC_{29} + nC_{31} + nC_{33})$ ; <sup>d</sup>carbon preference index =  $[(C_{25} + C_{27} + \dots + C_{33})/(C_{24} + C_{26} + \dots + C_{32}) + (C_{25} + C_{27} + \dots + C_{33})/(C_{26} + C_{28} + \dots + C_{34})]/2$ . The data for alkanes are from Duan et al. [24].

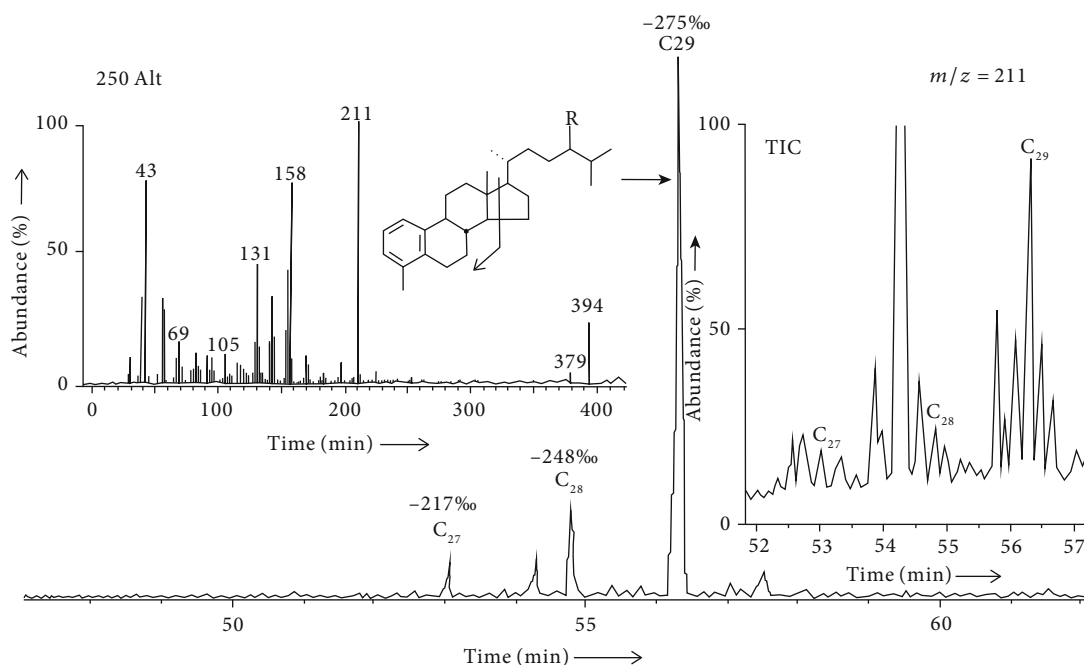


FIGURE 2: Molecular and isotopic distributions of ring A monoaromatic steroids in the 250Alt sample.

spectrum characteristics were almost the same as those reported by Hussler et al. [26]. Sedimentary ring A monoaromatic steroids are thought to be derived from sterols from organisms [26], and that the sterols in higher plants are composed mainly of C<sub>29</sub> components [27]. The distribution of the

ring A monoaromatic steroids in the sample was dominated by C<sub>29</sub>, reflecting the source of terrestrial higher plants. The limited detection of ring A monoaromatic steroids at 250°C in the thermal simulation sample indicates that these compounds only existed in the early stage of diagenesis [26].

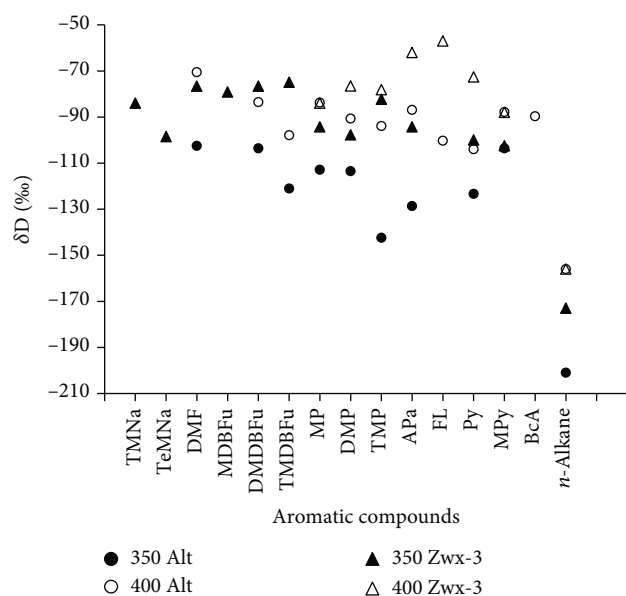


FIGURE 3:  $\delta D$  values of aromatic compounds in the pyrolysis samples (TMNa: trimethylnaphthalene; TeMNa: tetramethylnaphthalene; DMF: dimethylfluorene; MDBFu: methyl dibenzofuran; DMDBFu: dimethyl dibenzofuran; TMDBFu: trimethyl dibenzofuran; MP: methylphenanthrenes; DMP: dimethylphenanthrenes; TMP: trimethylphenanthrenes; APa: acephenanthrene; FL: fluoranthenes; Py: pyrene; MPy: methylpyrene; BcA: benz[c]acridine;  $n$ -alkane:  $nC_{16}$ – $nC_{31}$ ; mean  $\delta D$  value of  $n$ -alkane was reported by Duan et al. [24]).

In addition to the above-mentioned polycyclic aromatic hydrocarbons, the liquid hydrocarbons produced from the Zhanjiang peat also contained alkyl naphthalenes, dimethylpyrenes, and benzopyrenes. The PAHs in pyrolysates of Zhanjiang peat were still dominated by phenanthrene and its alkyl homologs, representing 53.2% and 48.3% of the total PAHs at 350°C and 400°C (named 350Zwx-3 and 400Zwx-3 samples), respectively, followed by pyrene compounds, which accounted for 17.1% and 24.0%, respectively. Relative abundance of chrysene and its alkyl homologs in the Zhanjiang samples were significantly higher than those in the Altay samples.

**3.2.  $\delta D$  Value of Aromatic Compounds.** The  $\delta D$  value of the PAHs produced by pyrolysis was shown in Figure 3. The  $\delta D$  values of the same type of the PAH compounds in Figure 3 were reported with average values of several peaks, such as dimethylfluorene, methylphenanthrene, dimethylphenanthrene, trimethylphenanthrene, and methylpyrene. The  $\delta D$  values of PAHs in the 350Alt and 400Alt samples were between  $-142\text{‰}$  and  $-92\text{‰}$  and  $-129\text{‰}$  and  $-66\text{‰}$ , respectively. The  $\delta D$  value of long-chain alkylbenzenes in the 350Alt sample was between  $-179\text{‰}$  and  $-113\text{‰}$  (Figure 1 and Table 3). The hydrogen isotope ratios of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  ring A monoaromatic steroids were obtained only in the 250Alt sample, which were  $-217\text{‰}$ ,  $-248\text{‰}$ , and  $-275\text{‰}$ , respectively (Figure 2). The  $\delta D$  values of PAHs in the 350Zwx-3 and 400Zwx-3 samples were between  $-103\text{‰}$  and  $-75\text{‰}$  and  $-88\text{‰}$  and  $-62\text{‰}$ , respectively.

TABLE 3:  $\delta D$  values of long-chain alkylbenzenes in Altay pyrolysis sample at 350°C.

Long-chain alkylbenzene	$C_{26}$	$C_{27}$	$C_{28}$	$C_{29}$	$C_{30}$	$C_{31}$
$\delta D$ value (‰)	-114	-174	-179	-141	-122	-113

## 4. Discussions

**4.1. Impact of Maturity on Molecular Composition and  $\delta D$  Value of PAHs Produced by Pyrolysis.** Although the PAHs in the Altay and Zhanjiang samples were dominated by tricyclic aromatic hydrocarbons (Figure 4), the difference in PAH composition between samples from the two areas was still obvious, showing that the Zhanjiang samples contained a high concentration of pyrene and its alkyl homologs as well as benzopyrene. Since these PAHs cannot directly originate from plants, they must be produced during the thermal simulation experiments. The difference in the composition of the PAHs throughout the thermal simulation process of the peat may be caused by the difference in the composition of the precursor substances that form PAHs in the peat from the two regions [28].

According to the results of our simulation, the ratios of  $P/(MP + DMP)$  and  $MP/DMP$  for the samples from Altay and Zhanjiang regions, respectively, were 0.044 and 0.456 and 0.133 and 0.534 at 350°C, respectively. At 400°C, these ratios increased to 0.086 and 1.027 for the Altay sample, and 0.144 and 1.107 for the Zhanjiang sample (Figure 5), respectively. These data indicated that demethylation of aromatic compounds occurs during thermal simulation. The abundances of 2-methylphenanthrene and 3-methylphenanthrene increased with increasing thermal simulation temperature relative to those of 1-methylphenanthrene and 9-methylphenanthrene (Figure 5), reflecting the progressive conversion of the  $\alpha$ -isomers to the  $\beta$ -isomers. The methylphenanthrene index (MPI) proposed by Radke and Welte [29] and Radke et al. [1, 2, 30] and the methylphenanthrene distribution fraction ( $F_1$  and  $F_2$ ) proposed by Kvalheim et al. [31] can be used as indicators of organic matter maturity. With an increase in the simulated temperature, these values in the samples increased significantly (Figure 5), reflecting that these values are strongly associated with the maturity of the organic material and supporting the previous research findings [1, 2, 29–31].

Previous studies have shown that the  $\delta D$  value of  $n$ -alkanes in sediments is well correlated with thermal maturity and can be regarded as an index of organic material maturity [24, 32]. Nevertheless, the correlation between the  $\delta D$  value of sedimentary individual aromatic compounds and thermal maturity is still unclear. The results of our simulation experiment showed that as the simulated temperature increased, the  $\delta D$  value of the PAHs produced by pyrolysis also increased (Figure 3). It was found that the PAHs at 400°C were, for the pyrolysates from Altay and Zhanjiang, respectively, 16‰–49‰ and 4‰–32‰ richer in D than they were at 350°C. They had an average enrichment of 27‰ and 14‰, respectively. Such a  $\delta D$  value variation between 350°C and 400°C should primarily reflect the influence of the thermal evolution of the organic material on the  $\delta D$  value of the PAHs. Therefore, the  $\delta D$  value of sedimentary

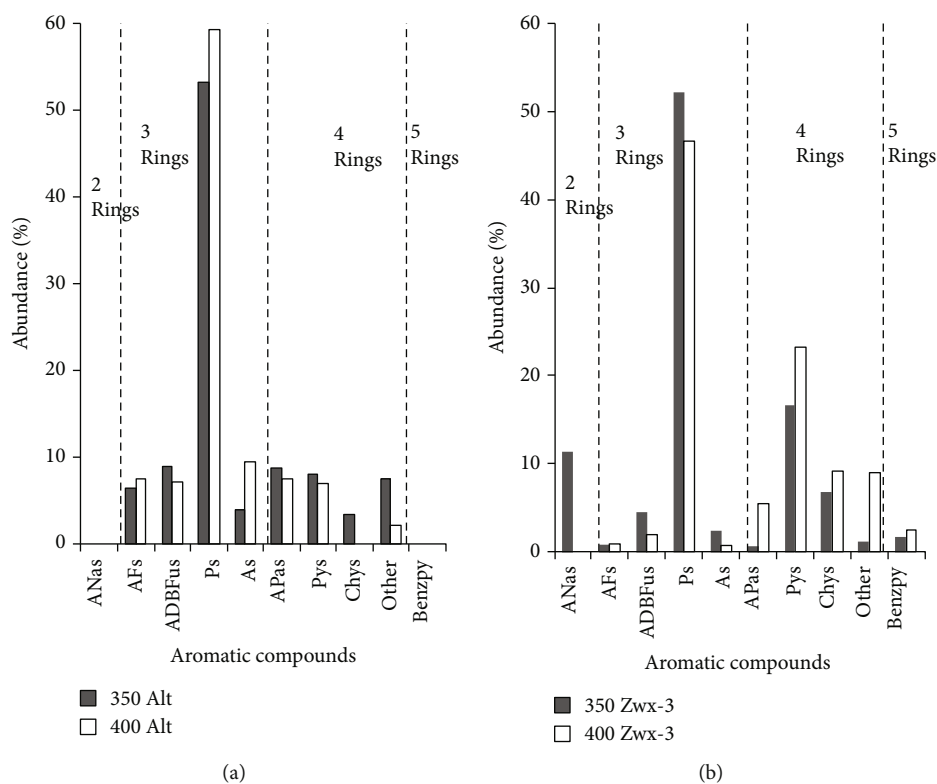


FIGURE 4: Compositions of PAHs in the Altay (a) and Zhanjiang (b) pyrolysis samples (ANas: alkyl naphthalenes; AFs: alkyl fluorenes; ADBFus: alkyl dibenzofurans; Ps: phenanthrene and its alkyl homologs; As: anthracene and its alkyl homologs; APas: acephenanthrene and its alkyl homologs; Pys: pyrene and its alkyl homologs; Chys: chrysene and its alkyl homologs; other: fluoranthene, benz[c]acridine, and benz[a]anthracene; Benzpy: benzo[e]pyrene and benzo[a]pyrene).

PAHs as an indicator of the maturity of organic material should be a scientific issue for future research.

Based on our previous results on hydrogen isotopes of hydrocarbon gases and *n*-alkanes in the studied samples [24, 25], the thermodynamic fractionation of hydrogen isotopes between the PAHs and both the hydrocarbon gases and *n*-alkanes was studied by comparison. At 350°C and 400°C, the  $\delta D$  values for methane obtained after pyrolysis were -318‰ and -272‰ in the Zhanjiang sample and -336‰ and -291‰ in the Altay sample, respectively [25]. Methane  $\delta D$  values in the Altay and Zhanjiang samples were significantly lower than those for PAHs (Table 4). The difference between the methane and average PAH  $\delta D$  values at 350°C and 400°C was -219‰ and -201‰ for the Altay sample, respectively, whereas Zhanjiang sample is -230‰ and -198‰, respectively [25]. At 350°C and 400°C, the average  $\delta D$  values of *n*-alkanes were -173‰ and -156‰ in the Zhanjiang sample and -201‰ and -156‰ in the Altay sample, respectively [24]. The PAHs had a higher  $\delta D$  value compared to that of the *n*-alkanes (Table 4). The average hydrogen isotopic composition of the PAHs at 350°C and 400°C was 84‰ and 66‰ and 85‰ and 82‰ heavier than that of the *n*-alkanes in the Altay and Zhanjiang samples, respectively.

**4.2. Impact of Climate Environment on  $\delta D$  Value of PAHs Produced by Pyrolysis.** At present, there are very few reports of hydrogen isotopes of PAHs in geological bodies. This

paper reported the  $\delta D$  value of the alkyl naphthalene, alkyl fluorene, alkyl dibenzofuran, alkyl phenanthrene, pyrene and methylpyrene, acephenanthrene, fluoranthene, and benzo[c]acridine PAHs in liquid hydrocarbons obtained from pyrolysis experiment of marsh peats from different environments. Due to the lower number of hydrogen atoms in each aromatic molecule, a greater amount of aromatic hydrocarbon sample is generally required for aromatic hydrogen isotope analysis. The simulated temperature points at only 350°C and 400°C had a large sample volume, which was used for aromatic hydrogen isotope analysis in this study.

As shown in Figure 3, at the same simulated temperature point, the PAHs in the Altay pyrolysis samples were enriched in H in comparison to the Zhanjiang pyrolysis samples. With the exception of methylpyrene and methylphenanthrene, their  $\delta D$  value discrepancy ranged from -60‰ to -19‰ at 350°C and -43‰ to -14‰ at 400°C, respectively, with an average difference of -29‰ and -16‰. The result also showed that the discrepancy in the  $\delta D$  values of the PAHs between the two types of samples becomes smaller with the increase of the simulation temperature.

Generally speaking, PAHs in sediments can come from natural (forest fires) and anthropogenic (fossil fuel) combustion [33–37]. However, as the Altay herbal marsh is situated in the uninhabited region of the plateau intermontane depression at an altitude of 2560 m, the human impact is minimal. At the same time, the plants in this area with a cold climate, an average annual temperature between -3.8 and

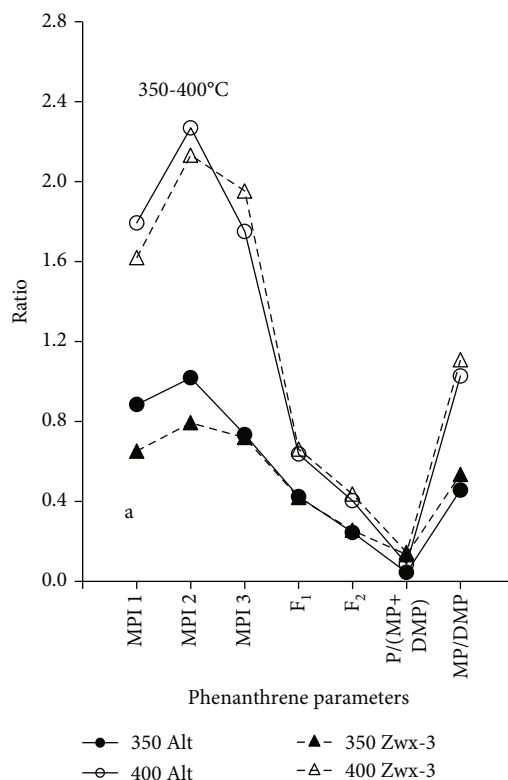


FIGURE 5: Distributions of phenanthrene parameter values in the pyrolysis samples (P: phenanthrene; MP: methylphenanthrene; DMP: dimethylphenanthrene; MPI1:  $1.5(2\text{-MP} + 3\text{-MP})/(P + 9\text{-MP} + 1\text{-MP})$ ; MPI2:  $3(2\text{-MP})/(P + 9\text{-MP} + 1\text{-MP})$ ; MPI3:  $(3\text{-MP} + 2\text{-MP})/(9\text{-MP} + 1\text{-MP})$ ; F<sub>1</sub>:  $(2\text{-MP} + 3\text{-MP})/(2\text{-MP} + 3\text{-MP} + 1\text{-MP} + 9\text{-MP})$ ; F<sub>2</sub>:  $2\text{-MP}/(2\text{-MP} + 3\text{-MP} + 1\text{-MP} + 9\text{-MP})$ ).

TABLE 4: Discrepancy in mean  $\delta D$  value between methane and PAHs, *n*-alkanes and PAHs, and PAHs in the pyrolysis samples.

Temperature (°C)	$\Delta_{\text{CH}_4\text{-PAHs}}$ (‰)	$\Delta_{\text{CH}_4\text{-PAHs}}$ (‰)	$\Delta_{n\text{-alkane-PAHs}}$ (‰)	$\Delta_{n\text{-alkane-PAHs}}$ (‰)	$\Delta_{\text{PAHs}}$ (‰)
	Alt	Zwx-3	Alt	Zwx-3	Alt-Zwx-3
350	-219	-230	-84	-85	-29
400	-201	-198	-66	-82	-16

D values of methane and *n*-alkanes were reported by Duan et al. [24, 25].

1.8°C, are almost entirely composed of herbal plants. The direct evidence for minor impact from anthropogenic input to PAHs was that except for benz[*c*]acridine, no polycyclic aromatic hydrocarbons were detected in the pyrolysis samples at 200°C and 250°C, and only traces of alkyl phenanthrenes and alkyl chrysenes were detected in the pyrolysis samples at 300°C. Therefore, in this study, PAHs formed by natural and anthropogenic combustion can be ignored. The main PAHs in the studied samples, such as alkyl naphthalenes, alkyl fluorenes, alkyl dibenzofurans, phenanthrene, and alkyl phenanthrenes, may mainly originate from the aromatization of plant lipids in the thermal simulation process [38, 39], since the changes in the relative concentration of some PAHs in the samples were related to thermal evolution (Table 1). The similarity of the variations in the relative content of aromatic compounds in the Zhanjiang and Altay samples with the simulated temperature showed that the PAHs in the Zhanjiang pyrolysis samples should have similar genesis to those in the Altay pyrolysis samples. Thence, the  $\delta D$  value of

the PAHs in the samples was primarily connected to that of the plant lipids that served as its precursors. It is usually considered that the  $\delta D$  value of plant lipids mostly depends on the kind of plant and water used for plant growth [40, 41]. The  $\delta D$  value of the source water is dominated by the geographical location and climate environment [42–44], showing that the  $\delta D$  value of precipitation in high latitude and low temperature areas is relatively low [42–44]. The organic material in the studied samples primarily comes from herbal plants, but the latitude and temperature of the two regions were significantly different, so that the  $\delta D$  value (-100‰) of precipitation in the Altay high latitude region was 47‰ lighter than that (-53‰) of precipitation in the Zhanjiang low latitude region. This would indicate that the  $\delta D$  values of PAHs in the studied samples may be related to those of water in the two areas. This finding suggests that the  $\delta D$  value of sedimentary PAHs, like the  $\delta D$  value of *n*-alkanes in sediments, can reveal the paleoclimate environment. This understanding also needs to be further confirmed by more studies in the future.

**4.3. Significance of Hydrogen Isotopes of Long-Chain Alkylbenzenes and Ring A Monoaromatic Steroids Produced by Pyrolysis.** Long-chain alkylbenzenes are widely present in sediments and crude oil. Their distributional characteristics and sources have been studied [45–47]. However, the  $\delta D$  value of long-chain alkylbenzenes has not been reported. The Altay pyrolysate at 350°C contains abundant long-chain alkylbenzenes, and their  $\delta D$  value was also obtained. The  $\delta D$  values of the  $C_{26}$ – $C_{31}$  long-chain alkylbenzenes differ significantly (Figure 1 and Table 3). Mean long-chain alkylbenzenes was 78‰ D-enriched relative to mean  $n$ -alkanes with the same carbon number (-218‰) [24]. This large isotopic difference implies that they may have different precursors, although the long-chain alkylbenzenes and  $n$ -alkanes in the sample come from herbs. This is coincident with the source result reflected by the distribution of the long-chain alkylbenzene and  $n$ -alkanes. The long-chain alkylbenzenes had a long carbon chain and obvious even-odd predominance, which were completely different from those of  $n$ -alkanes in the studied samples (Table 2) [24], reflecting that the long-chain alkylbenzenes and the  $n$ -alkanes in the sample have different origins. At the same time, it is not ruled out that aromatization contributed in high  $\delta D$  value of the long-chain alkylbenzenes. This is due to the fact that there is a large isotope fractionation in the decomposition of hydrogen from carbon-hydrogen bonds because the C-D bond has greater decomposition energy coincident with the C-H bond [48]. Additionally, it was also observed that when compared to PAHs, long-chain alkylbenzenes had a lower  $\delta D$  value. The  $\delta D$  values of the long-chain alkylbenzenes are, on average, 23‰ depleted in D compared to the PAHs. This isotopic difference may be caused by the difference in the precursor biolipids and the degree of aromatization between the long-chain alkylbenzenes and PAHs.

The hydrogen isotopic composition of the ring A monoaromatic steroids was the lightest in the aromatic compounds from the studied samples. The average value of the ring A monoaromatic steroids was 30‰ lighter than that of the  $n$ -alkanes in the studied samples [39]. The apparently low  $\delta D$  values of these steroids are generally believed to originate from isotopic fractionation during isoprenoid lipid biosynthesis [49]. Furthermore, the hydrogen isotopic composition of ring A monoaromatic steroids should be closely related to that of the precursor sterols because they are produced when ring A of the precursor sterols is aromatized during the early stage of diagenesis [26]. Chikaraishi et al. [40] measured the  $\delta D$  value of  $C_{29}$  sitosterol in free lipids extracted from plant leaves around Lake Haruna, Japan, and the values for leaves in summer and autumn were -245‰ and -252‰, respectively. Chikaraishi and Naraoka [50] also studied the  $\delta D$  value of  $C_{27}$ ,  $C_{28}$ , and  $C_{29}$  sterols in free lipids extracted from plant leaves, molds, and soils near Lake Haruna in Japan. The results showed that  $C_{27}$  sterol had a relatively high  $\delta D$  value, with an average of -217‰ in soils.  $C_{28}$  and  $C_{29}$  sterols had an average of -241‰ and -242‰ in the leaves and -241‰ and -240‰ in the soils, respectively. The  $\delta D$  values of the  $C_{27}$  and  $C_{28}$  ring A monoaromatic steroids in the studied sample were analogous to

that of sterols showed by Chikaraishi et al. [40, 50]. However,  $C_{29}$  ring A monoaromatic steroids have a lighter hydrogen isotope composition, and the reason is still unclear.

## 5. Conclusions

For the purpose of understanding the  $\delta D$  value and thermal evolution of individual aromatic compounds in sediment, we carried out an anhydrous closed pyrolyses on herbal peats from different latitude regions. The results showed that the differences in the composition and  $\delta D$  value of the PAHs between the samples from different latitudes were obvious. Although phenanthrene and its alkyl homologs predominated in the composition of the PAHs produced by pyrolysis in the samples from the two regions, pyrene and its alkyl homologs and benzopyrene were more prevalent in the samples from low latitude than those from high latitude. The isotopic studies revealed that the PAHs pyrolyzed by herbal peat from high latitudes have lower  $\delta D$  value than those from low latitudes, and the  $\delta D$  value of their polycyclic PAHs was related to those of their water. In the simulation process, the thermodynamic fractionation of hydrogen isotopes is obvious. The  $\delta D$  value of the PAHs increased as the simulation temperature increased. The isotope difference between samples from different latitudes also decreases with an increase in simulation temperature. Compared with the  $\delta D$  value of  $n$ -alkanes and methane produced by pyrolysis in the same sample, the  $\delta D$  value of the PAHs produced by pyrolysis was the heaviest. In the same sample, the mean  $\delta D$  value of the long-chain alkylbenzene produced by pyrolysis was lower than that of the PAHs produced by pyrolysis and higher than that of the  $n$ -alkanes produced by pyrolysis. The  $\delta D$  value of the A-ring monoaromatic steroids produced by pyrolysis was the lightest of all the aromatic compounds produced by pyrolysis, which should be derived from isotopic fractionation during isoprenoid lipid biosynthesis.

## Data Availability

The data supporting the findings of this study have been listed in the table in the paper.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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